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Computational Materials Theory: Optimizing the Use of the Electromagnetic Spectrum

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Introduction: The ability to computationally predict how materials respond to incident radiation is of immeasurable importance to practically every DoD and civilian technology. While applications are too numerous to list, they include spectroscopic remote sensing, infrared night vision technologies, X-ray analysis, magneto-resonance imaging, photovoltaic light harvesting, information transmission and storage, and quantum control of molecules. In principle, the ability to theoretically predict how molecules and materials respond to incident radiation has been in hand since the early days of quantum theory of materials. While more improvements are required and are on their way, today, due to long-term support of the Office of Naval Research and significant contributions from Navy researchers, scientists are able to computationally predict how materials interact with X rays, optical radiation, infrared and terahertz radiation, and extremely low frequency radiation such as that due to microwaves and static fields. Work discussed here pertains to the computational prediction of a material's ability to respond to radiation in the latter four frequency ranges.

A precise roadmap for success in this endeavor would have been difficult 40 years ago. In retrospect, we now know that it first required a very new, indeed Nobel-prize winning theorem on quantum theory (1964), which today is known as density-functional theory (DFT).[1] In essence, this ONR-supported discovery told us that the quantum aspects of nature were significantly simplified for environments, such as those found on Earth, where most molecules and materials are primarily found in their lowest-energy electronic state. While the discovery of DFT essentially told us that computational materials science and chemistry was simpler than previously thought, unveiling the simplicity was itself a second monumentally difficult task that required approximately 30 years of dedicated analytical work before a relatively accurate DFT method, now known as the generalized-gradient approximation (GGA), was developed by Perdew and tested by coworkers.[2] A third major task was to computationally implement and test these fundamental insights and to convert the understanding into software that would allow a larger group of scientists to harness the predictive powers of computational materials science. Through the last four decades, ONR has further fostered the development through broad support of university researchers. In parallel, NRL has maintained a world-class effort in this area. In addition to partially supporting and collaborating on tests of the now widely used GGA,[2] scientists in the Center for Computational Materials Science (CCMS) have developed and applied a wide variety of computational tools for performing DFT calculations on molecules[2,3] and bulk materials.[2,4]

Computationally Enhanced Vibrational Sensing: Approximately 10 years ago, fast methods for predicting the Raman, infrared, and terahertz response and spectra of molecular materials were developed in the CCMS.[5] This capability has impacted several recent DoD-relevant efforts for which the computational understanding of the interactions between radiation and materials has arisen during the last two or three years. An early joint theory and experimental application of this method demonstrated that physisorbed organic molecules on metal surfaces could be detached by coupling an infrared source to strongly bonded surface atoms.[6] In essence, this provides a generic approach for low-energy vaporization of small quantities of molecules that are adhered to a larger piece of inert material. From the standpoint of understanding the structure of a semiconducting neutron sensing material, the developer of these materials approached NRL-CCMS researchers to aid in characterizing the structure of the films.[7] Similarily, the vibrational spectrum of heavy diamond-like particles, found naturally in oil deposits and used for tracking oil spills and their origins, has recently been calculated by NRL researchers.[8] Also, work aimed at understanding the absorption spectrum and solar-induced charging of an organic photovoltaic molecule (see Figs. 7 and 8) has been performed in response to a computational challenge from the DoD High Performance Computing Modernization Office.[9] In addition, very unique codes for predicting how magnetic nanoparticles resonantly absorb and emit low-energy electromagnetic radiation in molecular materials have been developed in the CCMS.[10] The energy released, currently in the sub-THz range, may provide a key to future THz oscillators if the magnetic molecules may be further optimized computationally.

Future Challenges and Capabilities: Future fundamental developments at the intersection of computational materials science and electromagnetic sensing will further impact our capabilities in both civilian and military theaters. While NRL researchers are currently capable of determining what a material is by comparing measured and calculated vibrational and optical spectra, an important goal is to learn how to control the properties of a specific molecular material by optimizing the power distribution of an incident electromagnetic radiation source. Such a capability will allow for a variety of DoD-centric technologies, which range from lower-energy (i.e., lower-cost) synthesis of

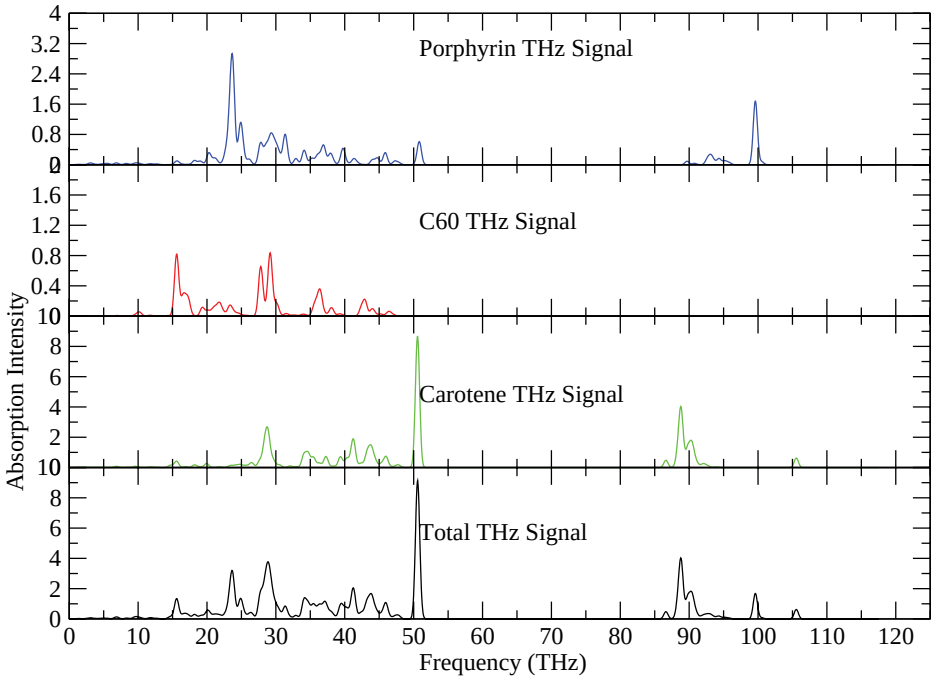

FIGURE 7
Density-functional-based prediction of charge-transfer state of a molecular photovoltaic.

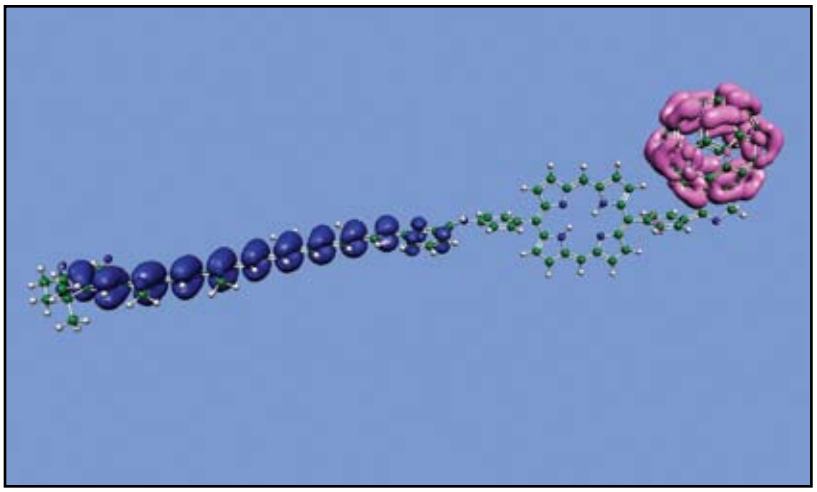

FIGURE 8
Density-functional-based determination of the THz spectra of the molecular photovoltaic depicted in Fig. 7. The weak signal in the 0 to 1 THz range underscores the fundamental scientific challenges that must be overcome to achieve sensing technologies in this energy range.

materials to sensing harmful materials. These two techniques, if combined, could possibly allow for simultaneously sensing and degrading or converting a harmful material. Conversely, for conversion of sunlight or other sources of electromagnetic radiation (such as that from lasers) into electrical energy or battery-charging applications, it is the materials properties that must be computationally controlled to optimize the efficiency of energy transfer. Solution of this fundamental problem could allow remote recharging of batteries. Work along these lines continues in the CCMS at NRL. Success along these lines will provide some of the new technologies required to respond to challenges of the near future.

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